Estimating the oxidative ratio of the global terrestrial biosphere carbon – the global terrestrial carbon sink has been underestimated.

Fred Worrall[11], Gareth D. Clay[1], Caroline A.Masiello[2] & Gabriel Mynheer[1]

1. Dept. of Earth Sciences, University of Durham, Durham, DH1 3LE, UK.
2. Dept. of Earth Science, Rice University, Houston, Texas, TX77005, USA.

Abstract

The oxidative ratio (OR) is the amount of CO_2 sequestered in the terrestrial biosphere for each mol of O_2 produced. The OR governs the efficiency of a terrestrial biome's O_2 production and it has been used to calculate the balance of terrestrial and oceanic carbon sinks across the globe. However, the value used in carbon cycle calculations comes from only one study of one environment. Here we perform a meta-analysis of studies of soil organic matter and vegetation composition to calculate the first global ecosystem OR value. We use data from 138 samples across 31 studies covering 9 USDA global soil orders, 7 global biomes and 5 continents and combine this information as a weighted average based upon biome land area or organic carbon content of the soil order. Organic matter fractions could not be shown to be reliable proxies for whole soil or vegetation OR. The resulting analysis suggests that although the presently used value of 1.1 is within the range of natural occurrence, it is likely not the most accurate choice, representing between the 97th and 99th percentile value. Our study yields a global terrestrial OR = 1.034 ± 0.032. This value of OR means that the sink of anthropogenic carbon fluxes to land has been underestimated (and the sink to the ocean overestimated) by up to 14%. Recalculating with our OR value, the fossil fuel carbon flux to land is 1.48 ± 0.06 Gt C/yr and flux to oceans is 2.02 ± 0.05 Gt C/yr.

[1] Corresponding author. Fred.Worrall@durham.ac.uk

Introduction

To estimate the relative global sinks of carbon it has become common practise to consider the relative changes of oxygen (O_2) and carbon dioxide (CO_2) concentrations in the atmosphere. This approach was first proposed by Keeling and Shertz (1992) and has subsequently been used to refine estimates of terrestrial and oceanic carbon sinks of fossil fuel emissions (Keeling et al., 1996). The approach of Battle et al. (2000) uses the following formula:

$$f_{land} = -\frac{1.43}{1.1} f_{fuel} + \frac{1}{(0.471 \times 4.8 \times 1.1)} \frac{d\left(\frac{O_2}{N_2}\right)}{dt} \quad \text{(i)}$$

$$f_{ocean} = -\frac{1}{0.471} \frac{d(CO_2)}{dt} - \frac{1}{(0.471 \times 4.8 \times 1.1)} \frac{d\left(\frac{O_2}{N_2}\right)}{dt} - \frac{1.1-1.43}{1.1} f_{fuel} - f_{cement} \quad \text{(ii)}$$

Where: f_x= the annual flux of CO_2 (Gt C/yr) with x= land, ocean, fuel or cement; (O_2/N_2) = the molar ratio of atmospheric O_2 and N_2. We take the sign convention that negative is loss to the atmosphere, i.e. f_{land} and f_{ocean} should both be positive. The constants in equations (i) and (ii) above are in the form as stated by Battle et al. (2000) except we have expanded certain constants to show where they derived from and where the OR term appears. In equations (i) and (ii) 1.43 is the “combustion stoichiometry”; 1.1 is given the name "photosynthetic stoichiometry”; 0.471 the conversion factor for Gt C to ppm CO_2; and 4.8 converts ppm to per meg. The photosynthetic stoichiometry is also known as the oxidative ratio (OR) and represents the ratio of moles of O_2 produced per mole CO_2 sequestered by the terrestrial biosphere – it is also known as α_B in the calculation of the atmospheric potential oxygen (APO – Stephens et al., (1998)).

Within the approach represented by equations (i) and (ii), the rate of change of (O_2/N_2) is estimated from observations of global atmospheric concentrations (Battle et al., 2000).

The flux from fossil fuels can be estimated from and was initially considered to have the largest source of error (Battle et al., 2000); however, it is also possible that there is variation in the OR term. Variation in the OR term can cause substantial variation in sink size calculations, but the value used for OR has received little scrutiny to date. The source of the value of 1.1 dates to the origins of the methodology, where the value of 1.1 was based on a study of the Biosphere 2 experiment (Severinghaus, 1995). This work did list a range of OR values based on literature, although no whole soil values were used, and the final estimate of OR was based on their own measurements in Biosphere 2. A range of studies (e.g. Langenfelds et al., 1999) have used single OR values instead of considering the breadth of ecosystem possibilities, and the results of this approach have been applied to global records (e.g. Battle et al., 2000), including the IPCC fourth assessment report (IPCC, 2007).

It is easy to demonstrate that changes in the value of OR can have consequences for the estimation of the terrestrial and oceanic carbon sinks: taking all values in equations (i) and (ii) to be as those stated by Battle et al (2000) and varying only OR shows that a 0.1 decrease in OR leads to 0.14 Gt C/yr change in f_{land}. When f_{land} is estimated as 1.4 ± 0.8 Gt C/yr, then an approximate 10% variation in the estimate of the OR value leads to a 10% change in the value of f_{land} (Figure 1). Similarly, a 0.1 decrease in OR leads to 8% change in the estimate of f_{ocean} (Figure 2).

The question arises whether a value of 1.1 for the global OR is appropriate. When OR is measured for individual ecosystems, values are rarely 1.1 and are not time-constant (e.g. Stephens et al., 2007; Gallagher et al., in review; Hockaday et al., in review). However, it is not possible to extract a globally-meaningful value from any one ecosystem study. To address this, we examine the global literature for terrestrial organic matter to determine the OR of the terrestrial biosphere's organic carbon and conduct a weighted analysis to determine the likelihood that 1.1 is the correct global value.

Approach & Methodology

Masiello et al. (2008) have shown that an OR value can be calculated from the elemental composition of terrestrial organic matter. In this study we combine new field data of the elemental composition of soils with literature values of elemental composition from soils and vegetation across the globe to provide the first global assessment of OR.

A value of OR can be calculated from a carbon oxidation state (C_{ox}), which can be determined from the elemental composition of organic matter as follows (Masiello et al. (2008):

$$c_{ox} = \frac{2[O] - [H] + 3[N]}{[C]} \qquad \text{(iii)}$$

Where: [X] = molar concentration of C, H, N or O. The OR value is the calculated as:

$$OR = 1 - \frac{C_{ox}}{4} + \frac{3[N]}{4[C]} \qquad \text{(iv)}$$

Equation (iii) assumes that there is no contribution to the C_{ox} from S or P, and it has been shown that the error in the OR of making such an assumption would be only ± 0.0002 , which is negligible compared to instrumental error (Hockaday et al., 2009). This error was added to the final calculation made in this study. Equation (iv) assumes that the ultimate source of N to each ecosystem is N_2: we considered this to be the most appropriate approach, because in addition to accurately representing the OR of ecosystems not receiving external fixed N, it also produces OR values very close to those calculated for ecosystems receiving the majority of their N in the form of NH_4NO_3 (e.g. agriculture) (Masiello et al., 2008). In the majority of cases the OR error of the N_2 assumption would be not more than 0.008 (Hockaday et al., 2009) – again we take this maximum error into account.

We reviewed the literature from 1975 to 2010, considering data if, and only if, they met the following criteria:

i) They were for whole soils or vegetation – humic or fulvic extracts were considered separately and compared to results for whole soils in case they could be used to boost samples sizes.

ii) Only soils from the topmost horizon or within 30 cm of the surface were considered – we assumed that deeper soils would be of less importance in considering recent exchanges of carbon with the atmosphere.

iii) Authors measured C, H, N and O concentrations – for reasons discussed below and for reasons of developing a suitable size of dataset we considered this the minimum data while if we had considered CHNOS data then the dataset would have been unacceptably small.

iv) The soils or vegetation could be clearly associated with a location and one of the soil or vegetation types listed below.

v) All data was derived from elemental analysis – we did not recalculate data from NMR analyses or from bomb calorimetry although we did accept values of C_{ox} from such methods wherever they had already been calculated as OR.

All the literature reviewed not cited directly in this text is listed in the Supplementary Material. The data from literature was supplemented with data of the CHNO analysis of peat soils at Moor House in northern England. The Moor House catchment is covered with ombogotrophic peat with a median depth of 2m (Clay et al., 2010). Within this catchment we took 6 cores from 6 different management types and sampled the peat at 2 cm increments to 30 cm depth. These peat soil samples were dried to 105°C and the CHNO concentration measured in a Costech ECS 4010 elemental analyser. These cores were taken not only to enhance the amount and breadth of data available to this study but also to assess the error

structure of OR data, i.e. assess the relative size of the sampling and measurement variance in a large dataset.

An examination of the literature showed that whilst there were relatively few studies that considered whole soil measurement, there were a larger number of studies that analysed some component of terrestrial organic matter, e.g. humic acid. Because of the relative availability of data for humic acids, fulvic acids, and dissolved organic carbon, these components were considered in comparison to the whole soil data in order to test whether this type of data could be used to extend the available information.

To estimate a global value of OR, we combined the available data for soils and vegetation using a stochastic weighted average. This stochastic weighted approach allowed us to consider multiple sources of error and variation in both the measured and calculated OR values as well as the errors in the estimates of weighting factors. We classified soils data into the USDA soil taxonomy orders (e.g. Inceptisols) except that we assumed that Gellisols were equivalent to Histosols, i.e. we considered 10 soil orders, not all 11 in the USDA taxonomy. We calculated the median and the reported range of the OR of each soil order wherever possible. Where that was not possible, we used the value for the median of all soil OR values and the maximum reported range of the measured OR. This conservative approach assumes nothing about the underlying distributions, given the size of the datasets when divided into soil orders. Instead of using the area of each soil order, we used the estimated organic carbon content of the soil orders (Eswaran et al., 1993), as this better reflects the larger terrestrial carbon stores in soils such as Histosols. The estimates of the organic carbon stored in each soil order are stated with an error range, and this range is used as the spread of the weightings within the weighted average. We then calculated the global soil OR as a stochastic combination of 100 randomly sampled OR values and biome areas from within the observed and defined ranges, assuming a uniform distribution within that range.

In a similar manner we considered the vegetation data as a stochastic weighted average where we classified data into one of 16 global biomes (Olden et al., 2001) and calculated their median and range. The organic carbon content of the 16 global biomes was not available, and so the weightings were taken as the estimate and error in the estimate of the areal extent of each biome (Loveland and Belward, 1997). We then calculated the global vegetation OR as a stochastic combination of 100 randomly sampled OR values and biome areas, as for the global soil OR estimate.

An estimate of the global OR of the terrestrial biosphere was then calculated using two approaches. In our first, the simplest approach, we made no attempt to correct for carbon pool residence time: we simply calculated a pool-weighted global OR average. In our second approach we attempted a basic weighting for carbon pool residence time.

First, the estimates of the global soil OR was taken as:

$$\mathrm{OR}_{\mathrm{terra}}^{\mathrm{global}} = \mathrm{P}_{\mathrm{soil}}^{\mathrm{terra}}\mathrm{OR}_{\mathrm{soil}}^{\mathrm{global}} + \mathrm{P}_{\mathrm{veg}}^{\mathrm{terra}}\mathrm{OR}_{\mathrm{veg}}^{\mathrm{global}} \quad \text{(v)}$$

Where: $\mathrm{OR}_{\mathrm{terra}}^{\mathrm{global}}$ = the oxidative ratio of the global terrestrial biosphere; $\boldsymbol{OR}_{\boldsymbol{soil}}^{\boldsymbol{global}}$ = the oxidative ratio of the global soils; $\boldsymbol{OR}_{\boldsymbol{veg}}^{\boldsymbol{global}}$ = the oxidative ratio of the global vegetation; P_{soil}^{terra} = the proportion of the terrestrial biosphere C reservoir that is found in soils; and P_{veg}^{terra} = the proportion of the terrestrial biosphere C reservoir that is found in vegetation. The value of $\boldsymbol{OR}_{\boldsymbol{terra}}^{\boldsymbol{global}}$ was the then calculated, as above, as a stochastic combination of the values themselves calculated stochastically as the median of 100 random selections from the ranges of OR and P values where: P_{veg}^{terra} = 0.28 and P_{soil}^{terra} =0.72 (Eswaran et al., 1993; Olson et al., 2001).

In our second approach, we allowed for the fact that C turnover in the vegetation reservoir is faster than in the soil reservoir, and therefore the $\boldsymbol{OR}_{veg}^{global}$ would be expected to be of greater importance than the size of the reservoir would suggest. Therefore, $\boldsymbol{OR}_{terra}^{global}$ is:

$$\mathrm{OR}_{\mathrm{terra}}^{\mathrm{global}} = \mathrm{f}_{\mathrm{soil}}^{\mathrm{terra}}\mathrm{OR}_{\mathrm{soil}}^{\mathrm{global}} + \mathrm{f}_{\mathrm{veg}}^{\mathrm{terra}}\mathrm{OR}_{\mathrm{veg}}^{\mathrm{global}} \qquad \text{(vi)}$$

Where: f_{soil}^{terra} = the proportion of the terrestrial biosphere C annual flux that is due to soils; and f_{soil}^{terra} = the proportion of the terrestrial biosphere C annual flux that is due to vegetation. We estimated the annual flux from the soils or vegetation as the size of reservoir divided by the average residence time. The average carbon residence time for soils is taken as between 20 and 40 years and 2 – 5 years for vegetation (e.g. Gaudinski et al, 2000). We recognize that the OR of soil fluxes and soil pools may not be identical (just as the carbon isotopic values of the bulk soil carbon pool rarely match the carbon isotopic values of the soil CO_2 flux). However, we must start with the assumption of equivalence between soil OR flux values and OR pool values because no data yet exist comparing soil pool and flux OR values. The value of $\boldsymbol{OR}_{terra}^{global}$ was then calculated, as above, as a stochastic combination of the values themselves calculated stochastically as the median of 100 random selections from the ranges of OR and f values: on this basis f_{soil}^{terra} = 0.27 and f_{veg}^{terra} = 0.73. The implications of the new estimate of the OR_{terra}^{global} are calculated through equations (i) and (ii).

Results

The cores at Moor House gave a range of OR values between 0.92 and 1.08 (n=60, Fig 3). The ANOVA of the OR values shows that there was no significant change with depth, but

there was a significant change between sampled cores: the standard deviation in OR across the whole dataset was 0.034.

A total of 39 studies gave rise to a dataset of 99 OR values, that covered 10 of the 11 soil orders (Ultisols were not represented and Gellisols were counted as Histosols) and covered the following continents: Asia, North America, South America, Europe and Australia but not Africa or Antarctica (Table 1, Fig 3).

This distribution of data suggests that 1.1 is an overestimate for OR_{soil}^{global} . Further, given this distribution of the data, a value of 1.1 would represent the 83th percentile. Given the stochastic weighted average after 100 random selections the median value is OR_{soil}^{global} = 1.055 ± 0.023, where the error is given as the inter-quartile range - given this data distribution, the value of 1.1 would represent the 99th percentile. We have assumed that the outcome is not biased by the larger number of data for Histosols in comparison to other soils orders by using a weighted average of the data as divided into the USDA soil orders. Equally, most data are still focused near values of 1.05, with or without weighting (Fig. 3).

The median of all vegetation data was 1.02 and a value of 1.1 would be the 98th percentile in this distribution. By weighted average this comes to OR_{veg}^{global} = 1.03 interquartile range of 0.02.

The ranges of OR for humic acids, fulvic acids and dissolved organic matter are given in Table 3. By using ANOVA it was possible to test between the distribution of OR values for soils, vegetation, humic acids, fulvic acids and dissolved organic matter and then use post hoc testing to assess whether significant differences exist between types of organic matter. The post hoc comparisons show that soils OR values were significantly different at $p > 0.99$ from all other organic matter types that could be considered (Table 4). Only two comparisons suggested a significant similarity and that was between vegetation and humic acid OR values and between fulvic acids and dissolved organic matter. However, the nature of the data and studies available to us meant that we could not make more direct comparisons as

there were no studies where vegetation, soil, soil organic matter fractions and dissolved organic matter were all analysed from the same location. This ANOVA provides no evidence that other types of terrestrial organic matter could be a reliable proxy for whole soil OR values.

The first approach for calculating OR_{terra}^{global} (Equation (v)) gives a value of 1.046 with an inter-quartile range (IQR) of 0.012, given assumptions regarding the N cycle and the S and P content of organic matter, this gives a value of 1.046 ± 0.029. Given equations (i) and (ii) and leaving all other terms as given in Battle et al. (2000) then f_{land} = 1.47 ± 0.04 Gt C/yr and f_{ocean} = 2.03 ± 0.04 Gt C/yr, i.e. values of the OR presently being used are underestimating these fluxes by between 14 and 5% respectively. For the second approach to calculating OR_{terra}^{global} (Equation (vi)) gives an OR value of 1.028 with an IQR of 0.015, given assumptions regarding the N cycle and the S and P content of organic matter, this gives a value of 1.034 ± 0.032. As above, applying this new value to equations (i) and (ii) and leaving all other terms as given then f_{land} = 1.48 ± 0.06 Gt C/yr and f_{ocean} = 2.02 ± 0.05 Gt C/yr, i.e. values of the OR presently being used are generating values for these fluxes that are in error by 6% respectively.

Discussion

The value calculated here is clearly not a perfect representation of global OR; however, it is the first to attempt to calculate a truly global OR value to replace the single-environment value that has been previously used (e.g. Langenfelds et al., 1999). This study covers a range of biomes and soil types, and shows that the presently used value of OR is unlikely to represent global conditions (indeed the original study (Severinghaus, 1995) never intended its measured value to be applied globally). Our work highlights where at a global scale we know very little about OR and so highlights targets for future sampling. Table 1 shows that we found no studies of Ultisols from which we could calculate an OR value and only 1 each

for Aridisols, Entisols and Oxisols. For global biomes (Table 2) there were four vegetative biomes where we found no information (closed and open shrublands, savannas and permanent wetlands), while we noted that information was available for 5 continents but none for Africa or Antarctica. Furthermore, we have used land area of biome or the organic carbon content of a soil order to weight the measured values of OR. Such an approach as used by this study implies that the difference between biomes or between soil orders is a dominant control upon OR – there is currently no evidence to either prove or disprove such an approach. Alternatively, the OR of a soil order maybe controlled by its management, climate, vegetation or both. None of these factors are entirely independent of soil order but, for example, in the UK there are peat soils (Histosols) that are presently being used for row-crop agriculture, forestry and sheep production. Further, the UK has peat soils that in a natural condition are forming under both sphagnum mosses and sedges. This wide diversity of use and formation maybe the dominant control upon ecosystem OR. If we understand what controls the OR of the terrestrial biosphere then we can assess better the OR_{terra}^{global} by recourse to the correct databases.

Furthermore, better constraints on the OR and C_{ox} of a range of ecosystems is likely to provide useful information for C cycle management. Initial observations suggest that C_{ox} is linked to the decomposability of organic matter, with more oxidized organic carbon decomposing more rapidly (Kleber, 2010). This is plausible, because C_{ox} reflects the demand for O_2 in organic matter oxidation, with more reduced compounds demanding more O_2. Although the atmosphere is not oxygen-limited, soils and marine sediments can be, and oxygen exposure time has been linked to organic carbon preservation in marine sediments (Hartnett et al., 1998). For terrestrial organic matter, litter bag experiments have shown that the fraction of terrestrial organic matter remaining after decomposition is more reduced than the initial biomass (Baldock et al., 2004).

Furthermore, if OR can be shown to differ significantly between types of environment then it becomes possible to target environments that would be more efficient at impacting

upon global atmospheres than others, i.e. those having a significantly lower OR. Two environments may have similar CO_2 sequestration but differ in their OR, and therefore differ in the impact of that sequestration upon the atmosphere, i.e. how much they affect the mole fraction of CO_2 in the atmosphere.

This study is entirely about the value of OR for the organic matter of the terrestrial biosphere at equilibrium and we have assumed that all samples represent their specific soil or biome at equilibrium. It has been shown that a cumulative decrease in the OR of net primary production (NPP) by 0.01 over a period of 100 years would create an O_2 disequilibrium of 0.0017 and require an increased land carbon sink of 0.1 Gt C/yr to balance global atmospheric O_2 and CO_2 budgets (Randerson et al., 2006). Disequilibria could be caused by a range of processes in the terrestrial biosphere (e.g. land use change, increased atmospheric CO_2, hydrologic cycle variations). At present, a disequilibrium in OR has yet to be demonstrated in the field, but it would be surprising if it did not exist given that we know that many land use changes, for example, cause large shifts in the total organic carbon content (e.g. deforestation – Achard et al., 2000).

The value of OR_{terra}^{global} found by this study suggests that the global terrestrial carbon sinks are larger than previously expected. This may mean that other estimates of the terrestrial carbon sink size needs to be examined, e.g. that from C isotopes (e.g. Battle et al., 2000). However, it should be noticed that if this study is performing the first ever global assessment of OR in equation (i) then it might also be timely to consider changes in the value of the 1.43 constant (the combustion stoichiometry) not because the composition of any fossil fuel has changed but because the global mix of fossil fuels has changed with continued economic development – a decline in the value of 1.43 to only 1.36 would cancel the change in OR_{terra}^{global} from 1.1 to 1.05 proposed by this study. Of course, a priori there is no reason why that the value of combustion stoichiometry would not be greater than 1.43 and therefore exacerbate the changes proposed in OR proposed here. It may prove possible to

develop national scale OR and combustion stoichiometry to better assess the efficiency of sequestration of greenhouse gas emissions.

Therefore, we would propose that although we have estimated the terrestrial biosphere OR for the first time we have also highlighted the shortcomings in our knowledge of this important property, and measurements specifically for OR can now be targeted to have the most impact upon our understanding. We need to understand what controls differences in OR between and within environments – is it climate, land-use, vegetation and/or combinations of factors? Do we need to know OR at a regional or national scale? What causes OR of an environment to change?

Conclusions

The study has compiled values of oxidative ratio (OR) of organic matter in the terrestrial biosphere in order to provide the first estimate of the global OR and thus re-estimate the flux of carbon to land and oceans. The study has shown:

i) The weighted average global soil OR is 1.055 ± 0.023 and the weighted average global vegetation value is 1.03 ± 0.02.

ii) The residence time-weighted global average OR of terrestrial organic matter was found to be 1.03 ± 0.03 which means that the present value used by the IPCC represents the 97^{Th} percentile of observed values.

iii) The re-calculated global terrestrial OR means that the global flux of carbon to the terrestrial biosphere is 1.48 ± 0.06 Gt C/yr and to oceans is 2.02 ± 0.05 Gt C/yr.

It is clear from this study how important the oxidation state of the organic matter of the terrestrial biosphere is but how little is known about what controls it.

References

Achard F, Eva HD, Stibig HJ, Mayaux P, Gallego J, Richards T, Malingreau JP (2002) Determination of deforestation rates of the world's humid tropical forests. Science 297: 999-1002.

Akramov Y (1981) Changes in organic matter in reclaimed solonchaks. Pochvovedeniye 3: 87-93.

Allard B (2006) A comparative study on the chemical composition of humic acids from forest soil, agricultural soil and ignite deposit Bound lipid, carbohydrate and amino acid distributions. Geoderma 130: 77-96.

Bagautdinov FY, Khaziyev FK, Shcherbukhin VD (1984) Polysaccharide fraction of humic substances from a typical chernozem and a gray forest soil. Pochvovedeniye 10: 28-32.

Baldock JA, Masiello CA, Gelinas Y, Hedges JI (2004) Cycling and composition of organic matter in terrestrial and marine ecosystems. Marine Chemistry 92: 39-64.

Battle M, Bender ML, Tans PP, White JWC, Ellis JT, Conway T, Francey RJ (2000) Global carbon sinks and their variability inferred from atmospheric O-2 and delta C-13. Science 287: 5462: 2467-2470.

Celi L, Schnitzer M, Negre M (1997) Analysis of crbroxyl groups in soil humic acids by a wet chemical method, fourier-transform infrared spectrophotometry, and solution-state carbon-13 nuclear magnetic resonance. A comparative study. Soil Science 162: 189-197.

Clay GD, Worrall F, Rose R (2010) Carbon budgets of an upland blanket bog managed by prescribed fire – evidence for enhanced carbon storage under managed burning. JGR-Biogeosciences 115, G04037.

Davis WD, Erickson CT, Johnston CT, Delfino JJ, Porter JE (1999) Quantitative fourier transform infrared spectroscopic investigation of humic substance functional group composition. Chemosphere 38, 2913-2928.

Eswaran H, Van den Berg E, Reich P (1993) Organic carbon in soil of the World. Soil Science Society of American Journal 57, 192-194.

Gaudinski JB, Trumbore SE, Davidson EA, Zheng S (2000) Soil carbon cycling in a temperate forest: radiocarbon based estimates of residence times, sequestration rates and partitioning fluxes. Biogeochemistry **51**, 33-69.

Grishina A, Morgun LV (1985) Elementary composition of humic acids in cultivated sod-podzolic soils. Pochvovedeniye 10: 31-39.

Hartnett HE, Keil RG, Hedges JI, Devol AH (1998) Influence of oxygen exposure time on organic carbon preservation in continental marine sediments. Nature 391: 572-574.

Hayes TM, Hayes MHB, Skjemstad JO, Swift RS (2008) Compositional relationships between organic matter in a grassland soil and its drainage waters. European Journal of Soil Science 59: 603-613.

Hockaday WC, Masiello CA, Randerson JT, Smernik RJ, Baldock JA, Chadwick OA, Harden JW (2009) Measurement of soil carbon oxidation state and oxidative ratio by C-13 nuclear magnetic resonance. Journal of Geophysical Research – Biogeosciences 114: G02014.

IPCC (2007) Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor & H.L. Miller (eds.). Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Keeling RF, Shertz SR (1992) Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle. Nature 358: 723-727.

Keeling RF, Piper SC, Heimann M (1996) Global and hemispheric CO2 sinks deduced from changes in atmospheric O-2 concentration. Nature 381: 218-221.

Kleber M (2010) What is recalcitrant soil organic matter? Environmental Chemistry 7: 320-332.

Kuz'Menio T, Pavlova MP (1981) Distribution of organic matter and macroelements in floodplain meadow biogeocenosis. Pochvovedeniye 6: 16-26.

Langenfelds RL, Francey RJ, Steele LP, Battle M, Keeling RF, Budd WF (1999) Partitioning of the global fossil CO_2 sink using a 19 year trend in atmospheric O_2. Geophysical Research Letters 26: 13, 1897-1900.

Loveland TR, Belward AS (1997) The international geosphere biosphere programme data and information system global land cover data set (DISCover). Acta Astronautica 41: 681-689.

Maie N, Watanabe A, Kimura M (2004) Chemical characteristics and potential source of fulvic acids leached from the plow layer of paddy soil. Geoderma 120: 309-3232.

Mao JD, Schmidt-Rohr K, Davies G, Ghabbour EA, Xing, B. (2000) Quantitative characterisation of humic substances by solid-state carbon-13 nuclear magnetic resonance. Soil science of America Journal 64: 873-884 (2000).

Martin M, Celi L, Bonifacio E, Nardi S, Barberis E (2006) Characteristics of soil organic matter in a limnic histosol of the alpine morainic system. Soil Science 171: 527-540 (2006).

Masiello CA, Gallagher ME, Randerson JT, Deco RM, Chadwick OA (2008) Evaluating two experimental approaches for measuring ecosystem carbon oxidation state and oxidative ratio**.** Journal of Geophysical Research – Biogeosciences 113: G3, G03010.

Neves-Fernandes A, Giovanela M, Esteves VI, Marta M, Sierra S (2010) Elemental and spectral properties of peat and soil samples and their respective humic substances. Journal of Molecular Structure 971: 33-38.

Olson JS, Watts JA, Allison LT (2001) Major world ecosystem complexes ranked by carbon in live vegetation: a database. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory.

Patti AF, Verheyen TV, Douglas L, Wang X (1992). Nitrohumic acids from Victorian brown coal. The Science of The Total Environ*ment* 113: 49-65.

Randerson JT, Masiello CA, Still CJ, Rahn T, Poorter H, Field CB (2006) Is carbon within the global terrestrial biosphere becoming more oxidized? Implications for trends in atmospheric O_2. Global Change Biology 12: 260-271.

Russell JD, Vaughn DJ, Jones D, Fraser AR (1989) An IR spectroscopic study of soil humin and its relationship to other soil humic substances and fungal pigments. Geoderma 29: 1-12.

Schnitzer M, Preston M (1986) Analysis of humic acids by solution and solid-state carbon 13 NMR. Soil Science Society of America Journal 50: 326-331.

Severinghaus JP (1995) Studies of the terrestrial O_2 and carbon cycles in sand dunes gases and in Biosphere 2. PhD thesis Columbia University.

Skrzypek G, Jezierski P, Szynkiewicz A (2010) Preservation of primary stable isotope signatures of peat forming plants during early decomposition – observation along an altitudinal transect. Chemical Geology 273: 238-249.

Stephens BB, Keeling RF, Heimann M, Six KD, Murnane R, Caldeira K (1998) Testing global ocean carbon cycle models using measurements of atmospheric O_2 and CO_2 concentration. Global Biogeochemical Cycles 12: 2, 213-230.

Shurygina EA, Larina NK, Chubarova MA, Kononova MM (1971) Differential thermal analysis (DTA) and thermogravimetry (TG) of soil humus substances. Geoderma 6: 169-177.

Tonoco P, Almendros G, Sanz J, Gonzalez-Vazquez R, Gonzalez-Vila JJ (2006) Molecular descriptors of the effect of fire on soils under pine forests in two continental Mediterranean soils. Organic Chemistry 37: 1995-2018.

Ussiri DAN, Johnson CE (2003) Characterization of organic matter in a northern hardwood forest soil by ^{13}C NMR spectroscopy and chemical methods. Geoderma 111: 123-149.

Table 1. The range and median values of OR for each of the USDA global soil orders, except Gellisols. Values in italics are assumed from the median and range of the rest of the dataset. Where: 1 = Hockaday et al. (2009); 2 = Neves-Fernandes et al. (2010); 3 = Skrzypek et al., (2010); 4 = Celi et al., (1997); 6 = Mao et al., (2000); 7 = Akranov (1981) ; 8 = Grishina & Morgun (1985); and 9 = Bagautdinov (1984).

Soil order	Study	Soils	Range of OR	Median	Total OC (Pg)[I]
Alfisols	4	1	1.07 – 1.11	1.10	127 ± 79
Andisols	4	1	0.95 – 1.12	1.03	78 ± 55
Aridisols	7	1	1.02	1.02	119 ± 71
Entisols	4, 6	2	1.04	1.04	148 ± 50
Histosols	1,2,3,4, 6, 8, this study	15	0.92 – 1.11	1.03	357 ± 107
Inceptisols	4	2	1.03 – 1.10	1.07	352 ± 246
Mollisols	4, 9	3	0.93 – 1.30	1.14	72 ± 33
Oxisols	1	1	1.06	1.06	119 ± 50
Spodosols	8	6	0.90 – 1.22	1.08	71 ± 30
Ultisols	-	-			103 ± 72
Vertisols	1	1	**0.96**	0.96	19 ± 13

Table 2. The range and median values of OR for each of 16 global biomes. Assumed values are given in italics either as zero where no biomass would be present or the median value and range of the rest of the dataset. Where: 1 = Hockaday et al., 2 = Masiello et al., (2008); 3 = Kuz'menio et al. (1981); and 4 = Baldock et al. (2004).

Global biome	Study	No. of studies	Range of OR	Median	Area (km^2)
Evergreen forest	1,2	2	1.06 – 1.07	1.07	18711540
Deciduous forest	1,2	2	1.03 – 1.13	1.08	5689975
Croplands	1,2	4	0.98 – 1.05	1.02	13786674
Woody savanna	2	1	1.03	1.03	7564185
Grasslands	2,3	12	0.78 – 1.02	0.97	11228552
Mixed forest	4	6	1.02 – 1.08	1.07	7256033
Cropland/Natural mosaic	4	5	1.02 – 1.07	1.05	14615809
Closed shrublands		0		*1.02*	23145948
Open shrublands		0		*1.02*	19485107
Savannas		0		*1.02*	9168489
Permanent wetlands		0		*1.02*	1331178
Urban		0		*1.02*	268986
Snow/ice		0	*0*	*0*	16573114
Barren		0	*0*	*0*	17731848
Unclassified		0		*1.02*	78742

Table 3. The range and median values of OR for humic, fluvic acids and dissolved organic matter. Values in italics are assumed from the median and range of the rest of the dataset. Where: 1 = Neves-Fernandes et al. (2010); 2 = Celi et al. (1997); 3 = Martin et al. (2006); 4 = Hayes et al. (2008); 5 = Mao et al. (2000); 6 = Schnitzer & Preston (1986); 7 = Russell et al. (1989); 8 = Shurygina et al. (1971); 9 = Davis et al. (1999); 10 = Patti et al. (1992); 11 = Akramov (1981); 12 = Grishina & Morgun (1985); 13 = Allard (2006); 14 = Maie et al. (2004); 15 = Ussiri & Johnson (2003); and 16 = Tonoco et al. (2006).

Soil order	Study	Soils	Range of OR	Median
Humic acids	1,2,3-5,6-10,11,12,13,15,16	74	0.88 – 1.12	1.03
Fulvic acids	1,3,14,15	27	0.82 – 1.26	0.91
Dissolved organic matter	3, 9	1 (3 rivers, 1 lake)	0.87 – 0.95	0.91

Table 4. Post hoc comparisons between OR values for soils, vegetation, humic acids, fulvic acids and dissolved organic matter. Values are reported as the probability of the difference between compared pairs being zero. Numbers underlined are those where the difference was significant at least at a probability of being zero.

	Vegetation	Humic acid	Fulvic acid	Dissolved organic matter
Soils	0.00	0.00	0.00	0.00
Vegetation		0.99	0.00	0.01
Humic acids			0.00	0.01
Fulvic acids				0.99

Figure 1. The predicted flux of carbon to the terrestrial biosphere (f_{land}) from equation (i) varying oxidative ratio (OR) while holding all other variables and parameters as given by Battle et al. (2000).

Figure 2. The predicted flux of carbon to the oceans (f_{ocean}) from equation (ii) varying oxidative ratio (OR) while holding all other variables and parameters as given by Battle et al. (2000).

Figure 3. Histogram of all results from field and literature studies for whole soils and vegetation.

Fig. 1.

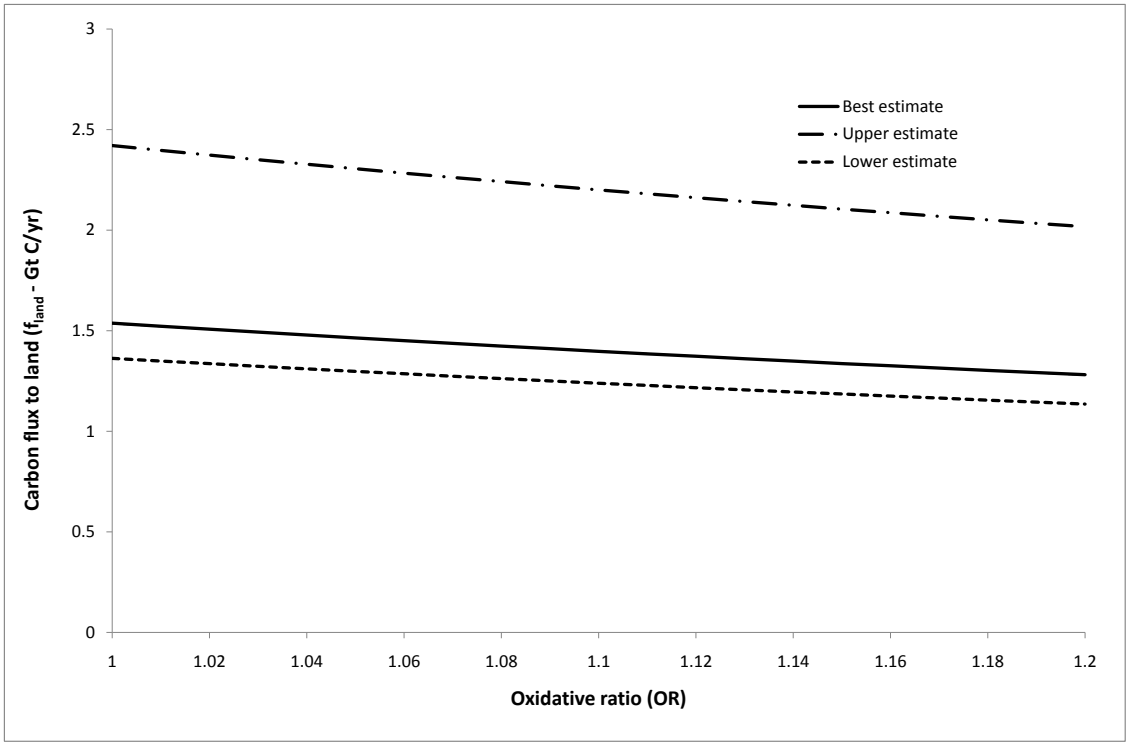

Best estimate
Upper estimate
Lower estimate
Carbon flux to land (f_{land} - Gt C/yr)
Oxidative ratio (OR)
3
2.5
2
1.5
1
0.5
0
1
1.02
1.04
1.06
1.08
1.1
1.12
1.14
1.16
1.18
1.2

Fig. 2.

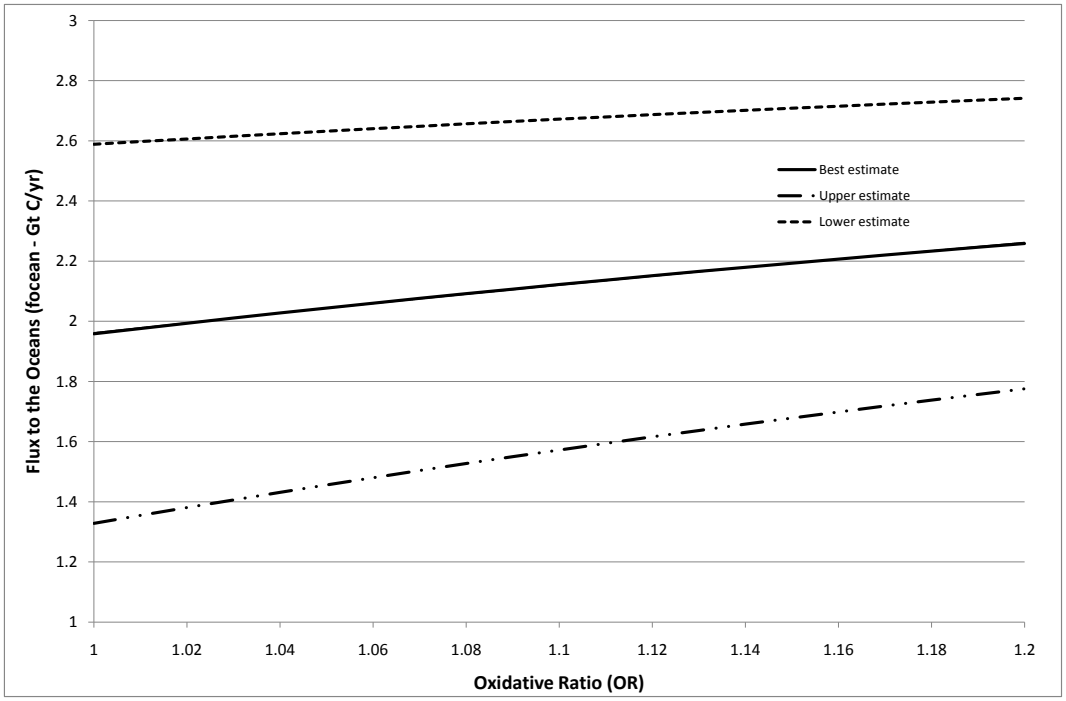
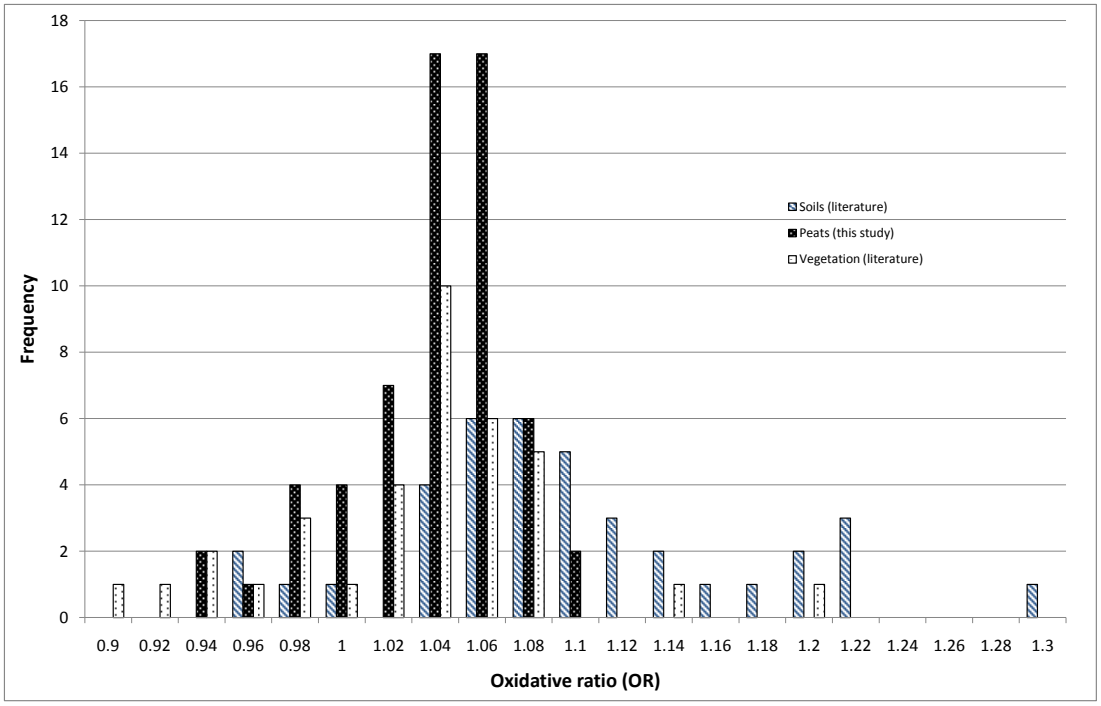

Flux to the Oceans (focean - Gt C/yr)
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
1
1.02
1.04
1.06
1.08
1.1
1.12
1.14
1.16
1.18
1.2
Oxidative Ratio (OR)
Best estimate
Upper estimate
Lower estimate

Fig. 3.



[i] Basen on Eswaran et al. (1993)